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Historical Article

Kuroda Chika (1884-1968) – Pioneer Woman Chemist in Twentieth Century Japan

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Abstract. Kuroda Chika was the first Japanese woman to graduate in chemistry. This article describes her early education and subsequent career in chemical research in Japan from 1913, and includes two years in Oxford (1921-1923). Her career as a researcher in The Physical and Chemical Research Institute (RIKEN) and as a professor at Ochanomizu University in Tokyo is described. Kuroda's organic chemistry studies, specifically the identification of the constitution of plant dyes is described. The status of female education and female employment in Japan during the first half of the twentieth century are also considered. Later in her career the achievements of Kuroda Chika were acknowledged with prestigious prizes and awards.

Keywords: Kuroda Chika, organic chemistry, plants dyes, chemistry in Japan, women scientists in Japan, Ochanomizu University, Tohoku University, RIKEN.

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Dedicated to the memory of Ms. Dr. Fukiko Tsuruki, biochemist, patent attorney and a good friend (1945-2020).

EDUCATION DEVELOPMENT IN KURODA CHIKA'S LIFE

Kuroda Birth to in Kyushu

Kuroda Chika was born in Saga, Kyushu Island, on 24 March 1884, the third daughter of her father Kuroda Heihachi and her mother Toku. Kuroda Heihachi 黒田平八 (1843-1924) participated in the samurai class rebellion known as the Saga Rebellion in 1874, and later served as a director of the Saga Rice Exchange 佐賀米穀取引所. He enabled his children, including his daughters, to receive a good education.

Education for girls in the late nineteenth-century Japan was rare. What drove Kuroda Heihachi to send his daughters to school in 1889? What was the social, educational and political situation in his town Saga in northwest Kyushu in those days?

The Need for a Better Education System

The realization of the need for a better, western influenced education, spread in Japan after 1853-1854 following the arrival of Commodore Perry's American party, which included the demonstrations of modern cannons in action and other technologies. The Japanese soon realised that they were far behind western countries in their technologies, and that they needed to acquire advanced techniques from the West in order to be able to compete with western countries and to prosper economically.

Kuroda Chika's life spanned the reigns of three Emperors. She was born during the Meiji Era (Meiji 1-45; 1868-1912) which stimulated the modernization of Japan; her education was during the Taisho Era (Taisho 1-15; 1912-1926); and her research and teaching was conducted during the Showa Era (Showa 1-64; 1926-1989). Those three eras, each one named after the corresponding emperors, represented the long road during which Japan progressed from a feudal country, with separate rulers in villages in remote domains, through changes in the national, military, political, and economic administration. After 1950 Japan became a world leader in its economy and several technological fields.

It is pertinent here to give a brief account of the major changes of the educational system.

Education System Revisions

In Edward R. Beauchamp's Introduction in *Japanese Education since 1945*, he observed that … "major attempts to implement basic educational systems occurred in the 1870s and again following World War II…."

In the section on "Japanese education, 1868-1945" Beauchamp explains that under the Meiji reformers "a highly centralized administrative structure with an emphasis on state-run normal schools was borrowed from France; a system of higher education rooted in a handful of elite public universities was the German contribution; the English model of Spartan-like, character-building preparatory schools stressing normal discipline which fit nicely into the Japanese context, and from the United States came the model of elementary education, a number of practical pedagogical approaches, and an interest in vocational education." (Beauchamp, 1994, pp. 3-4).

Beauchamp observed that "A second major reform period took place immediately following World War II as a key element of the Allies' determination to transform Japan from an aggressive military dictatorship into a peace-loving democracy (Beauchamp, 1994)." In the context of this reform, the Tokyo Women Normal High School in which Kuroda Chika studied and worked from 1907 became Ochanomizu University in 1949 and Kuroda was appointed a full professor of this university.

KURODA CHIKA'S LIFE HISTORY

Early Career

In 1899 (Meiji 22), aged five, Chika entered Saga town's Kanko Elementary School. She remained there until age 14 when she transferred to the Saga Girls Normal School (*Saga shihan joshi-bu*) for three years (in 化学史への招待 *Invitation to the History of Chemistry* 2019). During 1901 she served as a primary school teacher at another school in Saga and then moved to Tokyo.

In April 1902, Kuroda Chika entered the Division of Science of Tokyo Women's Higher Normal School (*Jokoshi*). Her chemistry teacher was Hirata Toshio. She graduated in March 1906. In the following month she was invited to teach at Fukui Normal School where she spent one year training teachers. Both Fukui Normal School and the Saga Normal Women's Department had the same principal who suggested that she should teach in Fukui, because he planned to establish a similar female science class at Fukui Normal School. She added that "the chemistry teacher was, of course, enthusiastic. The students were also enthusiastic, it was challenging, and it was fun and enjoyable." During 1907-1909 she completed her graduate course at the Tokyo Women's Higher Normal School and became assistant professor at the school. (Chika Kuroda Life History, Ochanomizu University digital research center p. 21).

She was first assigned to assist Professor Nagai Nagayoshi (1844-1929), who had studied chemistry and pharmacology in the laboratory of A. Wilhelm von Hofmann in Berlin.[1] Nagai's twelve years in Germany shaped his views in favor of women education. After returning to Japan in 1874, Nagai taught at the Department of Pharmacy, College of Medicine, Tokyo Imperial University, and at the Tokyo Women's Higher Normal School, where Kuroda Chika prepared demonstration experiments for his lectures. Nagai recommended that she take the entrance examination to Tohoku Imperial University in 1913, the year in which it opened its doors to women. She took the entrance examination with more than forty other people. Thirteen of them passed, including Chika and another woman, Tange Ume, both for chemistry studies. A director at the Ministry of Education sent a critical letter to the president of Tohoku Imperial University arguing against letting women start

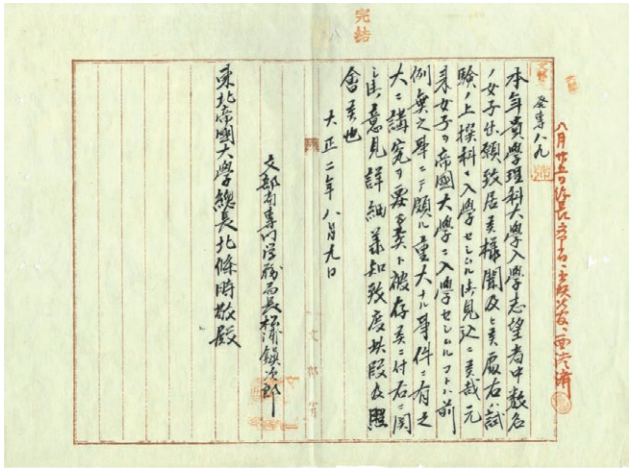

Figure 1. Hand written letter from the Ministry of Education to the President of Tohoku University 9 August 1913 (received from Tohoku University Library Archive 13.12.2020, publication permission 7.2022). On the right side of the letter, it is written in red letters that the President of Tohoku University went to the Ministry of Education to attend a meeting on August 25th. No record was made of what transpired at the meeting. (Courtesy of Tohoku University Archives).

Figure 2. Kuroda's photo legend: "Father and mother on their golden wedding anniversary and I (2nd row second from right) Tohoku Imperial University graduation commemoration." (Courtesy of Tohoku University and Kuroda Kotaro).

their education there, pointing out that it had never happened before (Fig. 1). However, Kuroda Chika was allowed to continue her studies and graduated in September 1916.

A copy of the hand written letter and its transcript is shown in Fig. 1.[2]

At Tohoku Imperial University, Kuroda Chika could choose from one of three chemistry professors: Ogawa Masataka (Inorganic Chemistry), Katayama Masao (Theoretical Chemistry), and Majima Riko (Organic Chemistry). Kuroda chose Professor Majima Riko as her instructor and advised him that she wished to study the constitution of natural coloring matters (Maeda Koko, Ochanomizu University digital research center publication p. 8).

In Kuroda Chika's memoirs written in 1957 she included a family photo taken in Saga in 1916, the year in which Kuroda Chika graduated (Fig. 2).

The photo (Fig. 2) shows everyone in traditional Japanese clothing. The father, Heihachi is sitting in the 2nd row, 4th from right, his wife Toku is next to him, 5th from right. Standing 5th from right is Kuroda Ryukichi 黒田龍吉, eldest son of Heihachi.[3] The parents are celebrating their golden wedding anniversary, which took place just after Kuroda Chika graduation of Tohoku Imperial University

After graduating from Tohoku Imperial University, Kuroda Chika returned to her alma mater, and taught at Tokyo Women's Higher Normal School. Concerning 1918 she wrote that "At that time, the influence of the First European War caused the status of science and engineering world in Japan to rise, and the chemical world was no exception." (Kuroda, 1957).

In another lecture in 1960, and article in 1961 she added:

> At that time, Professor Shibata Yuji took the lead at the University of Tokyo, saying, 'A Tuesday party was organized, and volunteers regardless of their university of origin held after their work, meetings once a month.' The venue was usually Enrakuken, in front of Todaimae, and the main purpose was to get to know each other.[4]

It was a lot of fun because it was both informative and encouraging, including discussions and souvenir stories." (Kuroda, (Ku-2012), 1961). This is a vivid description of the informal gathering organized by Professor Shibata with both young men and women from different universities; it was a relaxed and enjoyable social meeting.

Kuroda published her first article in 1918, in the journal of Tokyo Chemical Society (later the Chemical Society of Japan), presenting the results of her research under Majima's guidance. She managed to crystalize Shikon 紫根 *shikon/murasakine*, the purple root, gromwell root (of species *Lithospermum erythrorhizon*), and also established its structure (See Fig. 11 below). She named the color Shikonin. On 11 November 1918 she presented her findings in a lecture titled "About Purple Root Pigment" to the society. This was the first occasion when a woman addressed the society. (Kuroda, (Ku-1001), 1918). In 1918 she was appointed a professor at Tokyo Women's Higher Normal School.

THE OXFORD YEARS, MARCH 1921-AUGUST 1923

In 1921, Kuroda at age 37 was sent by the Ministry of Education to the University of Oxford in England, with the intention of working with Professor William Henry Perkin Jr. (1860-1929) on phthalonic acid derivatives. Perkin's response letter to Sakurai's letter of recommendation is kept in Ochanomizu University Archive. Perkin apologizes for not having a place for her, but nevertheless suggested that she should call for him later. Sakurai's letters to Perkin have so far not been found, but what is clear is that Perkin found a place for her to undertake research in 1921, apparently, in the new laboratory at Oxford (Appendix: Ku-4301).

Concerning Perkin's laboratory, Peter J. T. Morris quotes Jack Morrell's description of an organic chemistry laboratory built for Adolf Baeyer at Munich in 1877, which was a model for copying in England:

> …The [laboratory] system may have worked well, but it was probably liable to liberating volatile vapour into the atmosphere of the laboratory. It is perhaps not surprising that W.H. Perkin Jnr., a student of Baeyer who copied this arrangement in his laboratories at Manchester and Oxford, probably died of mercury poisoning. (Morris, 2015, Murrell 1993).

The transfer of the laboratory design to Manchester and Oxford is also mentioned in Kuroda's description of her conversation with Robert Robinson in Manchester prior to her return to Japan.

In her memories Kuroda tells how she enjoyed her time in Oxford and the hospitality of Perkin's family. During the two months' summer vacation she traveled to Europe. In Switzerland she climbed the Jungfrau Mountain and at the foot of Interlaken she gave a geography lesson at a primary school, telling the pupils "in a broken English" about Japan (Kuroda Memoirs 1957, (Ku-2006), -33- 72).

Japanese Students' Life Abroad in Nineteenth and Early Twentieth Century

Japanese students' stay in foreign countries involved overcoming a wide number of challenges concerning the difficulties of getting used to a different language, different food, daily customs and behavior (Cobbing 1998).

During Chika's stay in Oxford Albert Einstein was invited to Japan. In his recollections during the ship's sail to Japan he described his impression of the Japanese students in Berlin at that time:

> Never in my life have I been more envied in Berlin, and genuinely so, than the moment it became known that I was invited to Japan. For in our country this land is shrouded more than any other in a veil of mystery. Among us we see many Japanese, living a lonely existence, studying diligently, smiling in friendly manner. No one can fathom the feelings concealed behind this guarded smile. And yet it is known that behind it lies a soul different from ours… (Einstein, 1922, in Rosenkranz Ed. **2018**, 245).

Even though Kuroda Chika was a single Japanese woman in Oxford who had managed to come to terms with the different way of life in England, including accepting the way people looked at her, it seems from Kuroda's written memories that she had a pleasant stay in Oxford. It could be attributed to her good nature, as well as to that of her host, W. H. Perkin Jr.

Apart from a joint article with Perkin Jr. in 1923, very little can be found about her stay in Oxford in the English language. It is assumed that since her fellowship was paid by the Japanese Ministry of Education, she was not registered in Oxford University's records.[5] In her memories of 1957, in a photo taken at Oxford, Chika is dressed in a kimono, standing near a garden wall made of bricks, wood, and bushes (Fig. 3).

In Oxford, some months before Kuroda's return to Japan, one photograph (Fig. 4) shows in addition to Kuroda and Kato, sitting next to her, that there are six other Japanese men who were in Oxford at that time. In this case thirty-eight year old Chika is dressed in a western style and a hat. She wrote about her experience of putting on western clothes while she was on the ship going to England, sharing experience with her two younger cabin-mates. Kuroda Chika was elegantly dressed, in either kimono or western suit.

Kuroda recalled:

> Since Taisho 10 (1921), I spent two years in Oxford, England, supported by Prof. W. H. Perkin, who funded the research. In the research time Professor Robinson from Manchester University often visited Prof. Perkin. Just before I left England to return home I visited Professor Robinson at Manchester University. He invited me for a meal, I thanked him and I was told that the design of Prof. Perkin's laboratory in Oxford is the same as in Manchester. That was a comprehensive and an exceptionally memorable discussion (Kuroda (Ku-2012), 1961).

Kuroda included in her memoirs a photo of the boarding house at 139 Woodstock Road, Oxford, in which she resided (Fig.5). The boarding house owner was Mrs. Whitmarsh.[7]

Kuroda's memories from Oxford included:

Figure 3. (Ku-6016) Kuroda Chika in Oxford, Taisho11, 1922.

> Studying in the English Oxford University it is not easy to gain admission even for those who reside in the country. it is not easy to gain admission. But I am so grateful to Sakurai Jōji that I was enabled to undertake research. This was with the permission of Professor W. H. Perkin, the only professor of organic science at Oxford University, following a recommendation from Sakurai. For more than two years, I lived in the same room in a clean house in a scenic area; the laboratory faces the University Park next to Professor P [Perkin's laboratory]. I was able to continue my work in the room with an abundance of material, and I would like to thank Dr. P. [Perkin] for his generosity.

She concluded her memories, written in 1957, by adding: "During those two years, I had no time to become 'homesick'." Homesick she wrote in English, in katakana ホームシック (Kuroda、in Ocha. 1957 p.-33-72).

Figure 4. (Ku-6018). Taisho 12 January 26 (1923) in Oxford. Kuroda Chika and Japanese students.[6]

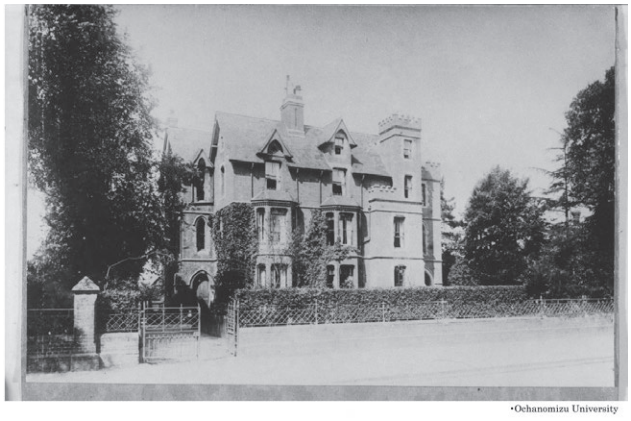

Figure 5 (ku-6017). Kuroda's boarding house on 139 Woodstock Road, Oxford (Ochanomizu University History Museum. Reproduced with permission).

BACK IN JAPAN

In August 1923, Kuroda's returned to Japan and her home in Saga, and then she reentered Tokyo Women's Higher Normal School. After the Great Kanto earthquake of September 1923 completely demolished the buildings of the school, Majima offered her a place in the Institute of Physical and Chemical Research (*Rikagaku Kenkyusho*, abbreviated RIKEN), founded in 1917.

Kuroda reflected: "Mr. Sakurai Norio (later, executive, doctor) guided me, but not only is the building and equipment comparable to those of foreign countries, but with air to each room pumped from a motor placed in the basement, etc. I was delighted to see that these standards in Japan had raised so much."

In RIKEN Kuroda continued her research and published her results under the title of "About the structure

Figure 6. Kuroda Chika, (Ku-6107), at age 40, at RIKEN, the Physical and Chemical Research Center, 1924. (Ochanomizu University History Museum. Reproduced with permission).

of safflower pigment" (Safflower (*Carthamus tinctorius L.*) (紅花の色素 *benibana no shikiso* 1929). This was her doctoral thesis. Original samples of her research materials are today held in Ochanomizu University Archives, (See Fig. 11).

Kuroda's Work Places: RIKEN > KAKEN > RIKEN

RIKEN was founded under a special government regulation and with financial support from the Imperial Household and private businessmen and companies. Facing financial difficulties after World War II it was reorganized in 1948 and was renamed KAKEN (*Kagaku Kenkyusho*, the Scientific Research Institute Ltd.). Kuroda Chika's affiliation was mainly RIKEN and then KAKEN for a few years (1949-1954). Further, after World War II, there was a new administrative reorganization, and in 1958 RIKEN assumed its original name *Rikagaku Kenkyusho*, and abbreviation, RIKEN (RIKEN,

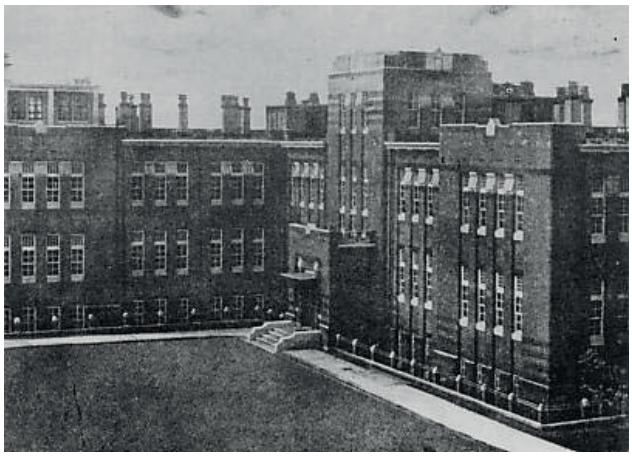

Figure 7. RIKEN building in Komagome, in northern Tokyo. (Reproduced with permission from RIKEN).

1983). It seems that since the 1920s Kuroda held a professorial, mainly teaching, position at Ochanomizu University, and had no facilities for chemistry experimental research. She used her RIKEN affiliation, to undertake experiments, as did other researchers, having more than one post at a certain time. Interestingly, in a publication of 1967, Kuroda's almost last article, co-authored with Okajima Masae, her affiliation is shown as the Department of Chemistry, Faculty of Science, Ochanomizu University, contributed by Yubata Teijiro. In this article Kuroda presented absorption spectra in the UV and visible ranges, infra-red spectra, as well as NMR spectra. This in accord with the progress of techniques in physical organic chemistry that were developed and used in those years.

Kuroda Chika's home was in Sugamo 巣鴨, in the northern part of Tokyo on the Japanese National Railway (JNR) train line, east of Ikebukuro 池袋. The map of Tokyo City shows that she could easily reach RIKEN, which was then located at Komagome 駒込 just one station east of Sugamo JNR rail station, or to Ochanomizu University, South-east of Sugamo. (Kuroda Kotaro. in *Invitation to Chemistry History* 2019).

Kuroda's Research and Teaching Colleagues

Kuroda's Research Partners

Kuroda's partners in research deserve their rightful recognition: firstly with her host professors in Japan's RIKEN, Majima Riko (1922); and in Oxford with W. H. Perkin Jr. (1921-1923). Then she published eleven articles during the years 1929-1931, and other articles as the sole author during the subsequent years. She collaborated

with the following researchers, according to her list of publications: Matsukuma Tokiyo (1932, 松隈ときよ 2 articles); Nakamura Teruko 中村照子 (1932, 2 articles); Mizu Wada 和田水 (collaborated during 1932-1938); Kisako Koyasu (1944); Umeda Masao (1949, 1951); Okajima Masae (1950, 1951, 1954, 1958, 1960, 1962, 1964, and 1967); and Harada Mie (1955). No students are mentioned who continued her line of research.

Kuroda's Career Progress and Teaching Colleagues

In 1929 (Showa 4th year) at 45 years of age, Kuroda Chika received the title Doctor of Science (D.Sc.), from Tohoku University. She received the 1st Majima Award from the Chemical Society of Japan in 1936. In 1949 Kuroda Chika became professor of the newly established Ochanomizu University, formerly the Tokyo Women's Higher Normal School (*Jokoshi*).

Kuroda's women colleagues at Ochanomizu University are shown in Fig. 8. The topics of higher education and of positions held by academic women in the first half of the twentieth century will be dealt with below. in 'Women Scientists in Early 1920s Japan'.

Kuroda's 1961 Speech (Ku-2012)

Kuroda's speech on the occasion of Majima's 88th birthday Showa 36 year, 21 May 1961. The 88th birthday is considered an important birthday in Japan. (Kuroda, (Ku-2012), 1961).

In her speech and published article, "Rice from the same Pot," おなじお釜のご飯, following the Majima's birthday lecture, Kuroda outlined the history of chemistry in Japan, starting with Udagawa Youan, who wrote books about botany and chemistry during the first half of the nineteenth century. Kuroda mentioned Udagawa Youan's book *Seimi Kaiso*, 舎密開宗 (Introduction to Chemistry), in which the author used Henry's original research work as the basis for a chemical book translated into Dutch and referring to similar books, along with his own experiences.[8] The Japanese nineteenth century scholar Udagawa Youan started botanical and chemical research after books from Europe that were imported to Japan (Endo et al., 2014. For Udagawa Youan see Siderer, in *Substantia* March 2021; Kikuchi and Siderer December 2021).

Kuroda further recollected: "The Chemical Society of Japan 75th anniversary meeting in 1953 was a very meaningful occasion, with the visit of Sir R. Robinson to Japan and other important events as mentioned above.[9] In recent years, the annual meeting reflects current trends in the development of chemistry." Robinson gave a lecture and other talks that I attended. I was happy to meet him and became more nostalgic. While I was a student in Sendai, and researched 紫根 Shikon, gromwell root, since about Taisho 5 (1916), reading carefully a joint paper by Professor P. and Dr. R. on natural pigment research, deepens my interest in plant dyes."

Robinson sent her Christmas cards every year, a special one in the year 1960: "Last year (1960) was very dif-

Figure 8. (Ku-6032). Faculty members of Ochanomizu University. Showa 25 about 1950. From right: 吉田武子 Yoshida Takeko, 黒田チカ Kuroda Chika, 保井コノ Yasui Kono 辻村みちよ Tsujimura Michiyo, 和田冨起 Wada Fuki. (Courtesy of Ochanomizu University).

Figure 9. (Ku-6033), Prof. Majima, Surrounding Prof. Katayama 片山先生 Showa 26 October 1951. Front row from left：辻村みちよ Tsujimura Michiyo, 黒田チカ Kuroda Chika (67 years old), 眞島利行先生 Prof. Majima Riko, 片山正夫 Katayama Masao, 片山正夫夫人 Mrs. Katayama Masao. Back row from right: 伊達たまき Date Tamaki, 山西貞 Yamanishi Tei, 岡嶋正枝 Okajima Masae, 鈴木照子 Suzuki Teruko, 吉田武子 Yoshida Takeko, 一人おいて leaving out one person, 小林ハナ子 Kobayashi Hanako.

Figure 10. (Ku-2012), 1961, 1163. Yoshinomiya and the author [Kuroda Chika] at the completion celebration venue of the Chemical Society of Japan Chemistry Library (Courtesy of Ochanomizu University History Museum).[12]

ferent in taste, and it was Dr.'s [Robinson] personality, humorous, ironic and impressive, so I will post it here." Robinson's appreciation of Kuroda Chika's research is reflected by his inviting her to Manchester University before she left Oxford to return to Japan; by his sending her annual Christmas and New Year greeting cards;[10] and by their meeting upon his visit to Japan in 1953. At the National Library of Israel in Jerusalem there is a copy of Robinson's comprehensive book following his lectures which he delivered on the occasion of the first Chaim Weizmann Memorial Lectures in Rehovot, Weizmann Institute of Science, Israel, in 1953. In this book he cited Kuroda's articles (Robinson 1955).[11]

Kuroda cited several of Robinson's works, including "VI. Notes on the characterization of the anthocyanins and anthocyanidins by means of their color reactions in alkaline solutions" for the use of specific solutions to change the pH of the dye under study (Robertson and Robinson 1928).

Kuroda continued her greetings "…By the way, what I would like to mention specially is the celebration of the completion of the Chemical Society of Japan's library on December 2, 1960. The honor and gratitude for being invited was inspiring, but at the same time, I was impressed with the deep joy and recounting of the history of Japanese chemistry." Kuroda's modesty and politeness is evident at the end of her 1960 speech, and in all her writings. In Fig. 10, during the celebration she wrote about, Kuroda is surrounded by scientists and other guests. One may see their appreciation to her.

Summary of Kuroda's Research Life Story

In dozens of articles Kuroda described detailed processes for isolation, crystallization and determination of the construction of the isolated dye crystals, extracted from plants and sea animal that were traditionally found and used in Japan. In 1936 she concluded that many of the extracts were derivatives of anthocyanin. In her memoirs written in 1957 Chika acknowledged and included photos of those scientists from whom she benefited: R. Majima, W. H. Perkin Jr., his brother G. A. Perkin, and R. Robinson.

It should be emphasized here that Kuroda Chika's research and achievements were on topics similar to those of the leading organic chemists in England, though there was far less support for laboratory facilities in Japan, and less recognition of her work.

She continued part time research and teaching as an emeritus professor after her retirement in March 1952.

Kuroda Chika started her memoirs by writing "Since I've learned about the endless world of academic study and the joy of walking that path, I was just drawn to the joy of discovering something I hadn't seen yet; and before I knew it, I had reached the age of 72. I am grateful that I still have enough energy to continue my research."

> At the end of last year, the research on substances in onion skin that act against high blood pressure which I had been working on for a long time, finally came to fruition, and it was transformed into the blood pressure medicine "Keltin C"; I am incredibly happy that it will be useful to many people, it will be my honor. (Kuroda (Ku-2006), 「化学の道に生きて)」 1957).

Recognition of Kuroda Chika's Achievements

In 1959 (aged 75) Kuroda Chika was awarded the Medal with Purple Ribbon (紫じゅ褒章, *shiju hōshō*), a type of Japanese medals of honor conferred by the emperor of Japan since 1955. In 1960 she was declared honorary president of the Society of Japanese Women Scientists. In 1965 (Showa 40) she was awarded the

Order of the Precious Crown, Gold Rays with Neck Ribbon 勲三等宝冠章受章.(Ochanomizu University Chika Kuroda's Life History p. 22).[13]

Kuroda Chika died in Fukuoka City, Kyushu, on 8 November 1968 (Showa 43), at 84 years of age. Her memory is cherished in Japan as a pioneering woman chemist.

Kuroda's Legacy for Young Women Students

Kuroda and her friend, the first woman biologist Professor Yasui Kono (1880–1971) established a prize for young students. They donated the celebratory money received at their retirement ceremonies (1952) to the school as part of the "Yasui-Kuroda Scholarship," which continues to encourage young researchers to this day (Ochanomizu University Library Website 2022).

New award carrying Kuroda's name was declared by Tohoku University.

The Kuroda Chika Award

> Every year, the Aoba Society for the Promotion of Science awards a selected few of female graduates who have produced outstanding achievements during their scientific doctoral studies. This award is given to female students selected from the whole doctoral cohort across the Graduate School of Science and the Graduate School of Life Science at Tohoku University. Named after Dr. Chika Kuroda, the first female to receive a chemistry doctorate in Japan from the Faculty of Science, the award was founded in 1999 to encourage female researchers in their scientific endeavors and careers. Over the last 15 years, 45 female students have been honored. (Received a link from Tohoku University 18.8.2022).

A statue of Kuroda Chika stands on the main street of Saga, alongside statues of other dignities of the city.[14]

Kuroda's Memorial Collections

Kuroda Chika's memorial collections are mainly stored in three institutes: (i) Ochanomizu University in Tokyo, where she studied and later taught; (ii) Tohoku (formerly Imperial) University in Sendai, where she started her academic chemistry studies in 1913; Kuroda's family donated her belongings to the archive in 2013 (reported in Mainichi shinbun 5 July 2013); (iii) and in RIKEN, where she pursued her research and published here articles. "Unfortunately, Kuroda Chika's materials before World War II were burnt in the war and only a few remain" (Kuroda Kotaro email, 11-12.4.2021).

KURODA CHIKA'S RESEARCH OF NATURAL PIGMENTS IN PLANTS AND IN A SEA ANIMAL

Early Studies of Plants in Japan

The study of plants has a long history in Japan. Eighteenth century herbal studies in Europe and in Japan were broadly reported in "Dodonaeus in Japan" (Edited by W.E. Vande Walle, co-Editor Kazuhiko Kasaya. 1998). The difficulties in translating Dodonaeus were explained by W.E. Vande Walle (Dodonaeus p.17). Eighteenth century writing in Japan about plants by Ono Ranzan (1729-1810) still referred to a Chinese book about plants. The introduction of western botany into Japan began with Udagawa Youan (1798-1846) and Ito Keisuke (1803-1901). Organic chemist Professor Majima Riko (1874-1962) started modern organic chemistry studies in Japan at the Imperial University of Tokyo. Majima had graduated in 1899 and became a graduate student of the department under the supervision of professor Sakurai. His generation was the first to study fully within a modern educational system. In 1903 Majima was promoted to the position of associate professor and was then sent by the Ministry of Education to Europe for further study. He conducted research in Kiel under Carl Dietrich Harries (1866-1923) and in Zurich under Richard Willstätter (1872-1942). Majima returned to Japan in January to the chemistry department at Tohoku Imperial University, a newly established imperial university in Sendai, northern Japan, in March 1911 (Kaji, 2015). Kuroda Chika was Majima's first student and later an associate; she continued studying organic chemistry and extended the knowledge of chemical studies of plants, specializing in plants dyes.

It should be noted that Kuroda's professors and mentors, Nagai Nagayoshi, Majima Riko and Sakurai Jōji, spent some years studying in Europe and brought to Japan their experiences, approaches to scientific research and instruments, from which Kuroda benefitted.

Kuroda's Scientific Publications

In the introductions of her articles Kuroda wrote short explanations for the reason to choose a certain plant in order to study its coloring material. These were certain historical or cultural explanations, mainly showing the Japanese background and occasionally the use of a plant in other parts of the world. Kuroda describes the analyses themselves by an accurate and concise way, without explaining the reasons for choosing a specific test method. However, she relied on many publications that dealt with similar materials, thus justifying their application in her further research.

In the following section, several of Kuroda's publications in which she specified the processes of chemical analysis and then the choice of synthesis in order to confirm the identity and formula of a certain extracted plant material are summarized.

As stated above, Kuroda published her first article in 1918, the result of her research under Majima's guidance. She crystalized Shikon 紫根, purple root (*murasaki*), gromwell root (of species *Lithospermum erythrorhizon*), and established its constitution and named the color Shikonin.[15] Another paper she published on this topic was with Professor Majima (Majima R. and Kuroda, C. (Ku-1002). *Acta Phytochimica*, 1922. Cited by Maeda, Ochanomizu University website).[16]

Interestingly, she returned to study the constitution of Shikonin in 1936 (Fig. 11). In her article, together with her female colleague of many years Dr. Wada Mizu, they crystalized Alkannin, the coloring matter of the root of Alkanna. They discovered the optical isomer of Alkannin, and that of Shikonin, having an asymmetric carbon next to carbon 3 of the ring. They decided that the Shikonin substance is a naphtazarin derivative, and not a naphtopurpurin, as Majima and Kuroda have previously suggested. Kuroda and Wada offered a proof based on synthesis for the constitution by synthesizing iso-hexyl-naphtazarin that had not been synthesized previously. Their product and Shikonin had the same melting point of 100°C and very similar elemental analysis, i.e., the relative amount of carbon, oxygen and hydrogen. Kuroda and Wada described the synthetic routes and characterized the intermediate compounds. Kuroda returned to the same molecule some eighteen years later. The relations between chemical analysis and synthesis are addressed below, following B. Bensaude-Vincent (Kuroda and Wada, (Ku-1031), 1936), (Bensaude-Vincent lecture 2021).

The Constitution of Carthamin

During the years 1929 to 1930 Kuroda Chika published several articles on "The constitution of Carthamin", the coloring material of Safflower flowers. It is a celebrated color in Japan and the petals contain both a yellow and a red dye. Crude carthamin paste was washed, dried, recrystallized from pyridine, giving several derivatives in order to detect the exact location of the hydroxyl group, and the nature of the color forming reaction. UV spectral data of the derivatives were given. (Kuroda (Ku-1004) 1929, Kuroda (Ku-1005) 1929, Kuroda (Ku-1006), 1929).[17]

Figure 11. (Ku-5001). Research results specimen kept by Kuroda: Shikon and Carthamin. Crystals and structural formula of Shikonin, Carthamin and Murasaki, Benibana (dry), purple dyeing. Experiments Materials: Murasaki – Root of Murasaki including pigment. Shikonin Research: gromwell root (of species Lithospermum erythrorhizon). Taisho 5th year ~Taisho 7th year. Safflower (Carthamus tinctorius); dyer's safflower. Carthamin research: Taisho 13th year – Showa 4th year. (Photo courtesy of Ochanomizu University History Museum).

The Constitution of Awobana

In 1931 a preliminary report on "The Coloring Matter of 'Awobana'" published by Kuroda Chika, discusses the flowers of *Tsuyukusa* 露草, *Commelina communis*. They are a beautiful azure blue from which were extracted blue fabric colorants, named Tsuyukusa or Awobana, meaning dew grass or a blue flower, respectively, commonly known as Asiatic Dayflower . "It is one of the most well-known and the oldest of its kind in Japan and the uses has a historical interest." (Kuroda (Ku-1014), 1931). Although not practical as a dye, it was still employed for drawing patterns in the art of Yuzen silk print and Shiborizome (tied dyeing). It is grown in some regions and used for paper dyeing by painting the flower extract on sheets of paper and drying in the sun, (thus) labeled Awobana paper." (Kuroda (Ku-1014), 1931, and (Ku-1022), 1933). Kuroda did not find an earlier record of this coloring material. She used the Awobana paper for the studies of the coloring matter constituents. Further studies on Awobana reported recrystallization; needle crystals were obtained from methyl alcohol.[18]

Anthocyanin Pigments

In a series of articles Kuroda reported her studies on *Kuromame* (black beans), *Shiso* and *Nasu* (eggplant)

and the constitution of each of the natural coloring matters that she named Kuromamin, Shisonin and Nasunin, respectively. By 1935 she combined her and Wada's research on these coloring materials. Kuroda states that she realized that the natural dyes that she studied were anthocyanins.

Anthocyanins are glycosides of anthocyanidins, the basic chemical structure of which is shown. (Wikipedia, accessed 24.3.2022).

Kuroda explained: "Kuromame", "Shiso" and "Nasu" are widely used vegetables in Japan, specially favored for their bright colors; therefore, the chemical study of their coloring matters is of great importance and of much interest. But almost no literature was found on the subjects. Kuroda and Wada were successful in isolating the main coloring matters in the crystalline states, and found that all three pigments were anthocyanins. Photographs of the different crystalline derivatives of each of the three dyes of Awobana were presented.[19] A detailed experimental section described all analytical steps, and color changes due to pH; Absorption spectra were measured. Following their earlier publication on each of those substances in 1933-1935 Kuroda and Wada combined their full findings in detail (Kuroda, (Ku-1030), 1936).

The Constitution of Kuromame, Black Soya Beans

> Kuromame, 黒豆, or black soya beans, belongs to *Glycine Soja Benth*, and is given the name because of its delicacy of taste and the especially deep bluish color of the seed-coat. It is used as a common food but is also served as one of the symbolic sweets in the typical ceremonial menu of the Japanese New Year. It is also favored as a medicinal substance, and especially recommended to vocalists Kuroda Chika and Wada Mizu (Ku-1030), 1936, p. 1). The black pigment was at first belived to be an anthocyanin. Kuroda and Wada gave the pigment the name Kuromamin to the crystalline glucoside of the pigment. In the mid-1930s, because it was suggested that different samples from different sources might have different derivatives as a result of their different appearances, the two researchers studied beans samples that they received from Manchuria (Mukaden and Shing Tai Tzu), which were under Japanese rule in those years, and showed that "the coloring matters of "Kuromame", regardless of the varieties and the localities, belong to the same kind of compound.[20] (Kuroda (Ku-1030), 1936).

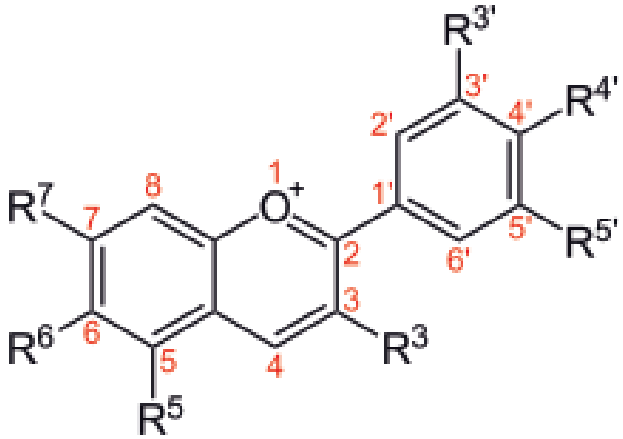

Figure 12. Anthocyanin.

Shisonin, the Coloring Matter of "Shiso"

The pigment of shiso 紫蘇 leaves (*Perilla Ocimoides L. var Crispa Benth*) (Japanese special name *Chirimen Shiso*) is extensively used in Japan for coloring "umeboshi", a kind of plum pickle. Kuroda and Wada studied the anthocyanin pigment obtained from the leaves cultivated in Tokyo. Following treatment with several solutions they found two substances that they labeled Shisonin A and Shisonin B. Shisonin was shown to be a mixture of two glucosides, Shisonin A and Shisonin B. Shisonin A was crystalized as its chloride; Shisonin B chloride was confirmed to be a compound of Shisonin A chloride and *p*-coumaric acid: the two components were isolated when Shisonin B chloride was treated with cold alkali in an atmosphere of hydrogen. (Kuroda and Wada (Ku-1030), 1936).

Nasunin, the Coloring Matter of Nasu (the Japanese name of eggplant)

Eggplant (*Solanum Melongena* L. *var esculentum Ness*) is a popular and useful vegetable food from summer to autumn in Japan; the color of its epidermis is noted for the beautiful dark purple which was used as a standard in dyeing in earlier times, called "Nasu blue." Kuroda and Wada were attracted to the study of its pigment. They found that it belongs to the anthocyanins and used the methods they have previously used for analyzing anthocyanin derivatives. "The isolation of the Nasu pigment in a crystalline state was extremely difficult; however, after several experiments a new crystalline glucoside which was named Nasunin by the authors who successfully obtained it as picrate, and finally as chloride. The Nasunin was shown to be 3-bio-di-glucoside of delphinidin", that is, an anthocianidin with two glucose derivatives attached to it.[21] (Kuroda and Wada, (Ku-1030), 1936, p. 283).

A beautiful, realistic drawing of Nasu was presented by the Japanese nineteenth century scholar Udagawa Youan, as depicted in his book of drawings (宇田川榕菴写生植物図譜).[22] As mentioned above, in her article "Rice from the same Pot" Kuroda mentioned Udagawa Youan's book *Seimi Kaiso*, 舎密開宗 (Introduction to Chemistry), "in which he used William Henry's original work as the basis for a chemical book translated into Dutch and referring to similar books, along with his own experiences." (Kuroda Ku-(2012), 1961).

Studies on the Derivatives of Naphthoquinone

Kuroda Chika's published articles include a series on "Studies of the Derivatives of Naphthoquinone", numbered from I- XVIII. Their subtitles refer to several sources of naphthoquinones, such as the pigments of Sea-urchins I-XIII, published during 1940-1967. Kuroda and her co-workers studied, analyzed and named seven different naphthoquinone derivatives that differed from each other by hydroxy or methoxy groups on the naphthoquinone rings or as side chains that determined the color, melting point, elemental and dissolution in different solvents. The long synthetic routes and the study of several kinds of sea-urchins received separate studies (Kuroda (Ku-1035) 1940, Kuroda (Ku-1048) 1953, Kuroda (Ku-1056) 1967).

In the final article in this series, published in 1967, Kuroda concentrated on *Pseudocentrotus depressus* (Ag.), the Japanese Aka-Uni or Hirata-Uni, a kind of sea-urchin unique to Japan. The shell, spine, and tube-foot of the sea-urchin are colored in dull red. The structures of four pigments labeled Spinochrome A to Spinochrome D were analyzed and presented. They were separated by column chromatography which gave three zones, colored violet, brownish red and green. They were examined by spectroscopic methods, including UV, visible spectra, infrared as well as NMR spectra. The use of NMR instrument method was not previously reported by Kuroda (Kuroda (Ku-1056), 1967).

The Outer Skin of the Onion Bulb, (1949, 1951)

Kuroda Chika's first article on "The Pigments and the Related Compounds in the Outer Skins of Onion Bulb" was published in 1949 (Kuroda, (Ku-1040), 1949).

The onion skin was used for dyeing yellow Easter eggs in Germany, and also alum dyeing of woolen, linen and cotton materials. "It was also used for dyeing in Japan in the home industry, giving brilliant golden yellow to commercial "alumite" (aluminum covered with its oxide)." (Kuroda (Ku-2006), 1957). Kuroda and co-author Umeda Masao stated that they wanted to continue and improve the earlier chemical study of Arthur George Perkin and John James Hummel (1896). After a tremendous amount of work they suggested that the yellow crystalline pigments obtained were quercetin, and continued the analytical identification of this matter. As described below, this research led Kuroda to the development of Keltin C, a drug used to treat high blood pressure.[23]

During research using the waste material of the outer skin of onion they confronted extraction difficulties, before they managed to obtain 100g of quercetin crystals, in December 1952. Kuroda filed four patents describing the process of extracting quercetin from the onion skin and making it into tablets, Showa 28- Showa 34 (1953-1959) (See appendix 2). Clinical trials were officially conducted, and it was confirmed that there were no side effects. In 1956 (Showa 31), a commercial product was released as "Keltin C" by the Japan-US Pharmaceutical Co., Ltd. In Kuroda Chika's memories she was thankful for the successful production of that drug (Kuroda (Ku-2006), 1957. Kuroda Kotaro 2019).

Concerning Kuroda's work, of which only some parts are mentioned here, the following questions come to mind. Were the methods that Kuroda Chika used the most recent methods of her time? In order to be able to answer these questions this author reviewed articles on similar topics of the same period.

KURODA CHIKA'S RESEARCH AND WOMEN IN SCIENCE IN JAPAN

In the following sections attention is given to two topics that arise from Kuroda Chika's career. They are: (1) Kuroda Chika's research in organic chemistry within the realm of organic chemistry in her time. (2) Women in science in Japan during the first half of the twentieth century.

Organic Chemistry

The following is a summary of the processes in chemical analysis and then the choice of synthesis in order to confirm the identity and formula of certain extracted plant's materials.

Organic Chemistry until 1960

Organic chemistry in the first half of the twentieth century was based on wet and dry methods, mainly

analysis, degradation and synthesis. Only after 1960 did instruments such as NMR, and mass spectra began to change the style of laboratory work.

The general approach is presented in Reinhard W. Hoffmann's book *Classical Methods in Structure Elucidation of Natural Products*. In his preface Hoffmann explains: "The structures of many natural products are depicted in standard textbook of organic chemistry as 'established facts.' But how certain are the experimental data that predicate a particular structure given for a natural product. In the case of natural products, the structures of which were elucidated in the period 1860-1960 by classical chemistry methods, the lines of evidence are frequently buried under a plethora of degradation studies, that is, investigations that repeatedly led into culs-de-sac and to revised structure assignments (Hoffmann 2014)."

Hoffmann's observation is reflected in Kuroda's approach, her extraordinary efforts and experiments to establish the correct identification of a substance.

A further example is Todd, on the work of Robert Robinson (Todd 1976). There are sections on anthocyanidins and anthocyanins. The chemical steps for elucidation the precursors of these molecules are described. Many years passed and many teams worked in order to decipher the constitution of materials, natural materials in this case, before the introduction of spectroscopic methods.

As for Japan, organic chemist Nakanishi Koji (1925- 2019), in *A Wandering Natural Products Chemist*, observed: "Organic chemistry in Japan in the early 1950s was undeveloped, and it would take 20 years before it reached a level approaching that of leading western countries. Monographs in Japanese on the electronic theory had just started to appear, but spectroscopy was still mostly unused." (Nakanishi 1991. p. 30). Nakanishi was working at Nagoya in early 1950s, and his description indirectly adds confirmation to the methods reported on in Kuroda's articles.

Analysis and Synthesis

For the various steps in isolations of a specific material one should bear in mind the importance of purity in order to enable identification. Indeed, there is no theoretical explanation by Kuroda as why she chose any route in her experiments. Her choices were based on intuition, knowing the relevant literature, and experience. Kuroda used synthesis in order to confirm her identification and characterization of the material she purified from plants' leaves. In order to validate the molecular structure she used synthesis in order to reach a molecule that resembles the molecule that she analyzed. Starting with molecular building blocks the synthesis progressed by steps until reaching the target product. This approach was used by Robinson and others (cited by Todd 1976, pp. 460-462).

It is of interest to refer to Bernadette Bensaude-Vincent 2021 reflection on analysis and synthesis: "The difference between synthesis and analysis rather emphasizes the significance of empirical knowledge, skills, tacit knowledge and tours de force. If synthesis complements analysis it is more as an exploratory method for discovery than as a method of proof to establish the true value of a hypothesis" (Bensaude-Vincent 2021).

In summary, the characteristics of laboratory life shed light on the work and results of Kuroda Chika's scientific research in her time, from 1916 to 1968: purity; crystallization; taking photos of various crystals' derivatives of the same parent molecules; [24] measuring melting points; elemental analysis; absorption spectra; and analysis and synthesis as complementing each other.

WOMEN SCIENTISTS IN EARLY TWENTIETH JAPAN

The following considers briefly the issue of women in science in Japan in the first half of the twentieth century. Kuroda Chika was a lecturer at Ochanomizu University and undertook her research in RIKEN. Even though it was a very successful career, one may wonder why the laboratory in RIKEN during those entire years was Majima's laboratory, even when he was engaged in Tokyo and only occasionally visited RIKEN. Kuroda's articles were submitted to journals by Majima or others. It is not clear whether this was a regular procedure.

Harrington on Women's Education

In 1987, Ann M. Harrington presented detailed documented information on the development of Imperial regulations concerning women's studies, starting in the Meiji era; the difference between the supporting rules that existed for lower level girls' studies, and hindrances of higher education for women. (Harrington. 1987).

Harrington shows that from 1871, there were several debates on the suitability for higher education for women, and though their conclusions were that even if it was favored, there was not Imperial regulation in support.

> In 1926, the question of women's education was dealt with in the House of Peers (upper house 1871-1947). It was argued that children possessed little economic sense because they were educated by mothers who do not have

> these skills. …Because of shortage of money… it was suggested again that co-education be tried. Against this suggestion there was "the assumption that men's and women's spheres are too different. Japan was not yet ready, it was argued, for a sudden change such as co-education. (Harrington 1987).

How are those events related to Kuroda Chika's career? We have seen that she could receive early education in her home town Saga, and a medium level education in Tokyo. As an intelligent and industrious student, she was recommended by Prof. Nagai to apply for the Tohoku Imperial University entrance examination in 1913. She was accepted and completed her studies, in spite of the Ministry of Education critical letter cited above. Nevertheless, Tohoku University did not enroll women to study for the next ten years. She undertook research in RIKEN for many years, but did not have a designated laboratory of her own. Perhaps this is the reason that we do not know of any student who worked with her and continued her work. So far, this author has not found any reference to Kuroda's complaining about this situation. On the contrary, in several instances Kuroda praised and was most thankful to those who helped her to pursue her research.

Scarcity of Research Positions for Women

The lack of higher studies by women implied fewer chances to undertake research. In 2008, Otsubo Sumiko described and analyzed women scientists' education, family, mentors, employment, and social activism. In the chapter on employment Otsubo states: "In the 1930s, talented women like Yasui (Kono), Tange (Ume) and Kuroda were all recruited by the women's schools from which they graduated. Although they were able to teach and earn a living, these schools more often than not lacked the facilities and funds to support their research. Thus, the women had to make special arrangements, such as using equipment at such institutions as Tokyo Imperial University and RIKEN, in the capacity of unpaid or poorly paid adjuncts." (Otsubo 2008. See also Kozai Y. et al. 2001). Significantly, the specific arrangements for Kuroda Chika in RIKEN during the years of her employment there are not described.

More recently, Furukawa Yasu has gathered information on seventy women who were born before 1920. He followed their educational history in Tokyo Women's Higher Normal School and Japan Women's College, and the role of RIKEN as a place for research. Furukawa considers the mechanism by which women could advance as researchers in the education system. Furukawa gathered statistics of those female studies: by birth, increasing in number from 1870 (2 researchers listed) to 1910-1920 (29 researchers listed); the school or university in which they attended, and the topics studied, e.g. logic, agriculture, humanities and sciences, science and technology and medicine. Furukawa mentions gender perspectives for specific topics chosen by female for their studies, but he gives no further elaboration on this point in these articles. (Furukawa 2020).[25]

Reports by the Chemical Heritage Japan (CHJ) Program

The Chemical Heritage Japan (CHJ) program of the Chemical Society of Japan was established in 2008. Its mission is to recognise world-class chemistry as part of the cultural heritage in Japan, from 2009, and disseminate information about its history, starting with Udagawa Youan's "chemistry –related materials including *Seimi Kaiso*" since 1820. By 2020 fifty seven reports related to academic, technical (manufacturing chemistry) and people had been published. About half of those are related to individuals. Arai Kazutaka thoroughly analyzed those reports. (Arai, in *Kagakushi*, The Journal of the Japanese Society for the History of Chemistry, 2021). Kuroda Chika's biography is briefly told on report no. 19, including her photo (Kuroda 2013). Kuroda Chika is the only woman who is included in these fifty seven short publications. While this certainly reconfirms her acknowledged achievements, one may wonder why there were no other successful women included in that list. For example: Sechi Kato (1893-1989), in 1931 she received a doctorate of science from Kyoto Imperial University, becoming the third woman to receive this degree. In 1942, at the height of the war, she was appointed to be a full-fledged research scientist, performing work on airplane fuels. In 1951 she became RIKEN's first female chief scientist, a position she held until her retirement in 1954 (RIKEN 2019 p.17); Michiyo Tsujimura (1888-1969), who became the first Japanese woman to earn a doctorate in agricultural science. She was appointed to a research position at RIKEN and later went on to become a professor at the newly established Ochanomizu University, a national university for women (RIKEN 2019 p.18); Ume Tange (1873-1955), an expert in food and vitamin chemistry (Furukawa 2021 p.315). More of their scientific career achievements are told in RIKEN's 2019 publication. Were their names considered for getting a CHJ report and dismissed or not considered at all is not known to this author.

NOTES

1. "Nagai Nagayoshi (1844-1929) was a pioneer elder of chemistry and pharmacology in Japan. He was a student at the University of Berlin, where he studied physics, botany and chemistry, and then undertook research in A. W. Hofmann's laboratory on organic chemistry, between 1870-1884; In Meiji 17 (1884) after 14 years in Germany he returned to Japan. In Tokyo Imperial University Nagai joined the physics and medicinal chemistry departments, and was in charge of teaching. Moreover, in Meiji 34 he was in charge of home chemistry at the Faculty of Home Economics, Japan Women's College." (*The Chemical Society of Japan, 2003. A 125-year Quest for Excellence 1873-2003.* Kikuchi and Siderer, 2021).

2. Transcript of the hand written letter and its printed version (received with thanks from Tohoku University Library Archive; and email from Tohoku University Archives):
本年貴学理科大学入学志望者中数名ノ女子出願致居候様聞及ヒ候処右ハ試験ノ上撰科ニ入学セシムル御見込ニ候哉　元来女子ヲ帝国大学ニ入学セシムルコトハ前例無之事ニテ頗ル重大ナル事件ニ有之大ニ講究ヲ要シ候ト被存候ニ付右ニ関シ御意見詳細承知致度此段及照会候也
大正二年八月九日 Taisho 2nd year (1913) 9 August
文部省専門学務局長　松浦鎮次郎
Ministry of Education Specialized Academic Affairs Bureau Director Matsuura Shigejiro
東北帝国大学総長　北条時敬殿 President of Imperial Tohoku University Houjou Tokiyuki.

3. Kuroda Kotaro email to Y. Siderer, 4 February and 21 November2021.

4. Enrakuken was a fashionable western-style restaurant situated diagonally across from the red gate of Tokyo Imperial University.

5. "The only reference I have been able to find to Dr Chika Kuroda is in a pamphlet entitled 'The Development of Organic Chemistry at Oxford, Part 1' by JC Smith where two Japanese students are mentioned as under the supervision of 'Clemo'…. As far as I have been able to discover, Clemo may refer to George Roger Clemo, a DPhil student within the department at the time." (Correspondence with the Bodleian Library, Assistant Keeper of the University Archives 30 March 2021).

6. (Ku-6018) Members in Fig. 4. 加藤文雄 Kato Bunyuu is in the center, near Kuroda, celebrating his going to Manchester University as a foreign student. He was apparently a foreign student of Nichiren Buddhism. Other persons in the photo, from left to right:田中寛一（Tanaka Kanichi) Tokyo Higher Normal School (Presently University of Tsukuba); 神保格 (Jinbou Kaku) Tokyo Higher Normal School; 手塚 ？ (Tezuka ?) army major; 皆川正禧 (Minagawa Masaki) Mito High School (Presently Ibaraki University) 島村盛助 (Shimamura Morisuke) Yamagata High School (Presently Yamagata University); 田中秀央 (Tanaka Hidenaka) Kyoto Imperial University. Hidenaka Tanaka appears to have studied at Oxford, but we do not know about the others. (Ochanomizu University History Museum, email, 6 June 2022)

7. The address of the dormitory is verified in the Lodging House Delegacy list held by the Bodleian Library of Oxford University. "I have now had a chance to look through our records of the Lodging House Delegacy with mixed success. The records confirm that Mrs. Whitmarsh was a lodging house keeper at 139 Woodstock Road but we do not hold any records which list the names of the tenants who resided there at any period." (Correspondence with the Bodleian Library, Assistant Keeper of the University Archives. Another source revealed that the house is no longer standing there (Anne and Phillip Harries, email of 26.8.2021).

8. In this article Kuroda outlined the history of chemistry in Japan, starting with Udagawa Youan of Tsuyama domain, who, she continued, "from a translation of an original book from the Englishman [William] Henry and also added his own experience he compiled his chemistry book *Seimi Kaiso*. However, he was not teaching in school." She wrote about the distinguished Japanese scholars and important events during the years.

"However, the content seems to have been extracted from the writings of Sakurai Jōji and Majima Riko." (Email correspondence with Information Development Section librarian, Ochanomizu University Library. 4.11.2021).

9. A photo of Robinson presenting his lecture in Japan in "around 1953" is included in Nakanishi's book, **1991**, 31.

10. Kuroda received New Year greeting cards from Robinson each year; she reproduced the cover image of the 1956 card and the 1960 card, in her 1957 and 1961 memoirs, respectively. The 1956 image is a drawing of a large building; on its reverse is in hand "Sir Robinson laboratory", with laboratory written in kanji. It is not clear which laboratory it was. The 1960 greeting card that Kuroda refers to shows a monk with a simple telescope looking out through a window. Three more cards were recently found in Tohoku University archive, and will be discussed elsewhere. Robinson sent his cards to her university or home address: Dr. C. Kuroda 5-990 Komagome Toshsima-Ku, Tokyo, Japan.

11. In his 1955, book following his 1953 lecture, Robinson referred to Kuroda Chika's work by her name on p. 42. He cited her work on Carthamin (XLIII drawing)

from *Carthamus tinctorius* (Safflower) on p. 39: Ref. 87 p. 130 Kuroda C. Proc. Imp. Acad. Tokyo, 1929. **5**, 32, 82, 86.

12. "The library was closed in 2002 because the number of users decreased due to the improved availability of books in various universities." (Kuroda Kotaro email, 8.3.2022).

13. The Order of the Precious Crown (宝冠章, *hōkanshō*) is a Japanese order, established on January 4, 1888 by Emperor Meiji of Japan. Since the Order of the Rising Sun at that time was an Order for men, it was established as an Order for Women. (Wikimedia 29.10.2022)

14. Link to Monument of Great Figures (Spot 8) Pioneers of engineering and scientific fields Shida Rinzaburo/Kuroda Chika: http://saga-travelsupport.com/en/spot/detail.html?id=1163

15. Ocha 1. 学術論文リスト論文 p. 32. Ref. (Ku-1001), (in Japanese), 紫根の色素について、 Concerning purple root pigment 東京化学会誌、 **1918**, 39, 1051.

16. A list of Kuroda's publications in Ochanomizu University website numbered (Ku-x0yz). https://www.lib.ocha.ac.jp/archives/en/researcher/kuroda_chika.html?grid=txtlink

17. Carthamin is a natural red pigment derived from safflower (*Carthamus tinctorius*), earlier known as carthamine. It is used as a dye and a food coloring. Safflower has been cultivated since ancient times, and carthamin was used as a dye in ancient Egypt. It was used extensively in the past for dyeing wool for the carpet industry in European countries and to create cosmetics for stylish women, geisha, and kabuki artists in Japan, where the color is called Beni (紅). After 1859-60, it competed with the early synthetic dye fuchsine as a silk dye. (Wikipedia 30.10.2022).

18. *Tsuyukusa* 露草. A photo of the flower is shown in Ran Levy's book *Wild Flowers of Japan*, *A field Guide* **1995**, p. 150. Recently, the author of this article found the same flower in her garden.

19. In Kuroda's article on The Constitution of Awobanin and Awobanol (1936), (Ku-1029), p. 267 she included crystals' photos of: Fig.1 Awobanin picrate; Fig. 2 Awobanin A chloride; Fig. 3 Awobanin aglucone.

20. "The 'Kuromamin' was found to be identical with chrysanthemin, namely, cyaniding 3-monoglucoside. It took a long procedure. … Melting point 182°C and several methods used to decide the place in which the glucose molecule is attached. Absorption spectrum of Kuromamin chloride and chrysanthemum chloride also proved to be quite identical**…"** (Kuroda and Wada, (Ku-1026), 1935).

21. For the formula of delphinidin, see: https://www.frontiersin.org/files/Articles/746881/fnut-09-746881-HTML/image_m/fnut-09-746881-g005.jpg

22. In Udagawa Youan's album of plant drawings 榕菴写生植物図譜 *Youan shasei shokubutsu zufu* the eggplant, called Nasu in Japanese, and its flowers are beautifully depicted. One can appreciate the strong purple color that attracted Kuroda Chika to investigate the chemical nature of its pigment.

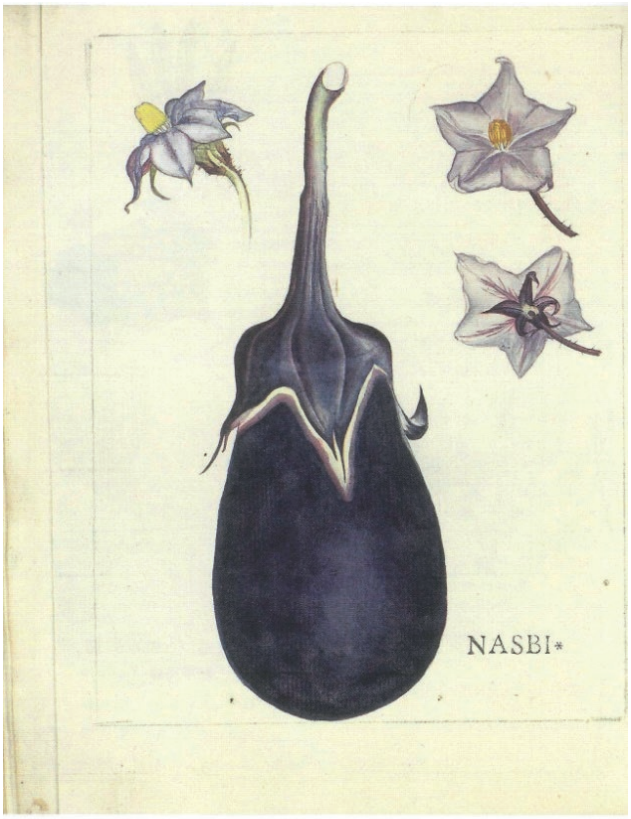

図 74（38b）ナス（*Solanum Melongena* L. var. *esculentum* Nees　ナス科）
「NASBI ＊」と印字（木活字）されている。

Figure 13. Udagawa Youan's eggplant painting (Endo et al. 2014, p. 611) (Photo courtesy of Takeda Science Foundation).

23. Kuroda's description of the steps to produce Keltin C.

"After re-examining the literature, I read that A.G. Perkin found that the onion skin contained 2% crecetin. Onion skin has long been used as a dye in Europe. Ruthin contained in buckwheat, etc. It was known that the glycoside of crecetin was effective in treating hypertension, but the November 1951 issue of Pharmaceuticals, which was read during the New Year holidays in 1952 (Showa 27), from a report in the magazine, I intui-

tively thought that crecetin obtained from onion skin would be used as a hypertensive agent…."
"Although 1 kg of skin was used every day in the experiment, it was only 10g in a basket cup, and it was extremely difficult to obtain multiple outer skins every day, but there was also the effort of many collaborators at this time." (Kuroda Ku-2006, 1957).

24. For instance, in her article on "The Constitution of Awobanin and Awobanol" (1936), (Ku-1029) p. 267) Kuroda shows photos of crystals of: Fig.1 Awobanin picrate; Fig. 2 Awobanin A chloride; Fig. 3 Awobanin aglucone.

25. Furukawa Yasu seminar handout of 8 December 2020, titled: 東工大火ゼミ 2020.12.8 資料 日本における女性科学者の誕生：戦前期研究者の経歴からの一考察 古川 安 *Birth of Female Scientists in Japan: A Study from the Career of Prewar Researchers* (in Japanese).

APPENDICES

Appendix 1. W. H. Perkin Jr.'s Letter to Professor J. Sakurai concerning Kuroda Chika, Oxford, 23 December 1920

Transcription of Prof. W.H. Perkin writing to Professor J. Sakurai Oxford December 23 1920:

Organic Chemical Laboratory
South Parks Road
Oxford Dec. 23 1920

Telephone
Oxford 423
Dear Professor Sakurai
A new hurdle, sorry that I should be
delighted to work with so distinguished
a Japanese lady, as Miss Chika Kuroda
if I had a vacant place in my laboratory
but unfortunately every place is taken.
However I am building a large new laboratory
It will be ready next summer and then I
can take Miss Kuroda and help her with
her work. Perhaps the best plan
will be for her to call on me when she
gets to England & we can then handle
matters over. During the last year
[page ends]

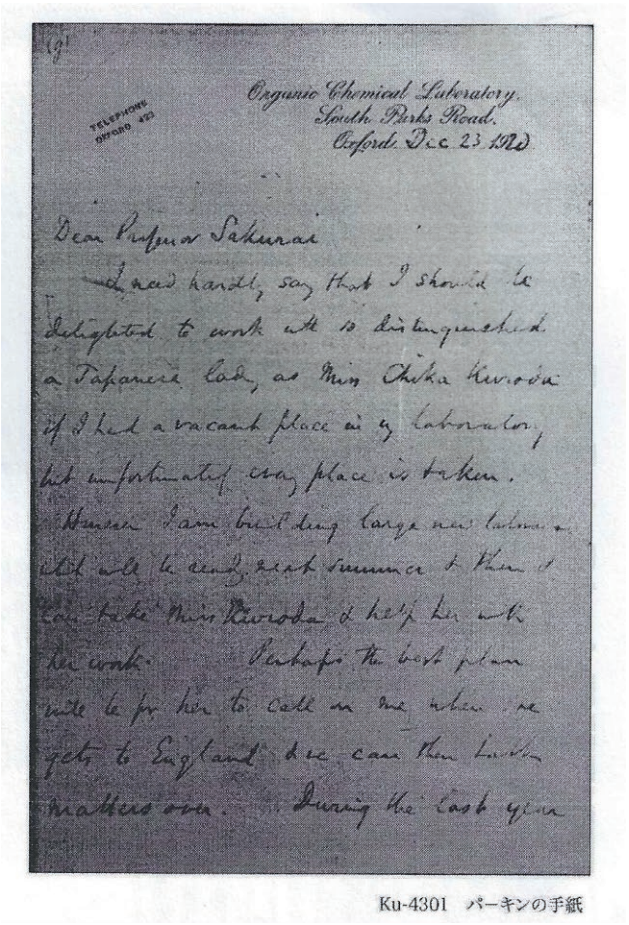

Figure 14. (Ku- 4301), W. H. Perkin Jr.'s Letter to Professor J. Sakurai concerning Kuroda Chika. December 23 1920.

Appendix 2. Kuroda Chika's first patent for the extraction of material from the outer skin of onion, 1953. Chemical structures in the patent seem to suggest how chemicals in an onion skin change in the baking process

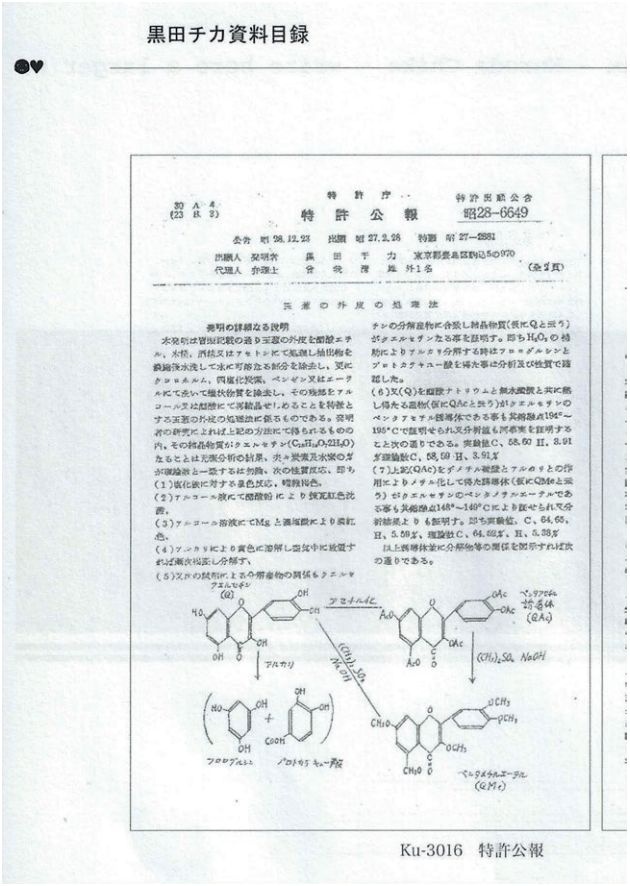

Figure 15. (Ku-3016) Kuroda patent 1953 玉葱【たまねぎ】の外皮の焼瑾法 "the way to bake an onion [and make it] like a beautiful ball".

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